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## NMR STUDIES OF METHANOL TRANSPORT IN MEMBRANES FOR FUEL CELL APPLICATIONS

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*Characterization of the methanol diffusion process in Nafion 117 was achieved with the use of a modified pulsed field gradient NMR technique. To ensure that the concentration of methanol was constant throughout the entire experiment, the membrane was continually immersed in the methanol solution. When using the standard pulsed field gradient NMR method, the diffusion of the methanol in the membrane is strongly influenced by the diffusion of methanol in solution. Application of a filter gradient suppresses the signal from the methanol in solution, enabling the methanol diffusion in the membrane to be observed unambiguously. Complete suppression of the solution signal was achieved when a 60% filter gradient was employed. Under such circumstances, the coefficient for diffusion of methanol within the membrane was calculated to be  $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , which is similar to the values reported in the literature. Consequently, the use of NMR filter gradient measurements is a valid method for studying the diffusion coefficient of methanol within fuel cell membranes.*

### Introduction

The performance of direct methanol fuel cells (DMFC) is not only dependent on the oxidation and reduction characteristics, but also on the nature of the transport processes within the polymer electrolyte membrane. Protons, which are a product of the methanol oxidation, are transported across the membrane where they react with oxygen to form water. Thus, it is essential that the membrane is an excellent proton conductor. In most cases, however, the membrane is also permeable to unreacted methanol, allowing it to crossover to the cathode. This reduces the overall performance of the cell

through inefficient use of the fuel and the development of a mixed potential at the cathode (Scott, 1999). Crossover can be kept to a minimum by lowering the methanol concentration (Ravikumar and Shukla, 1996; Scott et al., 1997, 1999). Alternatively, different membranes that are relatively impermeable to methanol can also be considered (Pivovar et al., 1999; Kreuer, 2001; Kerres, 2001). By developing a comprehensive understanding the nature of the methanol transport under different membrane conditions, the operating conditions for the fuel cell can be refined.

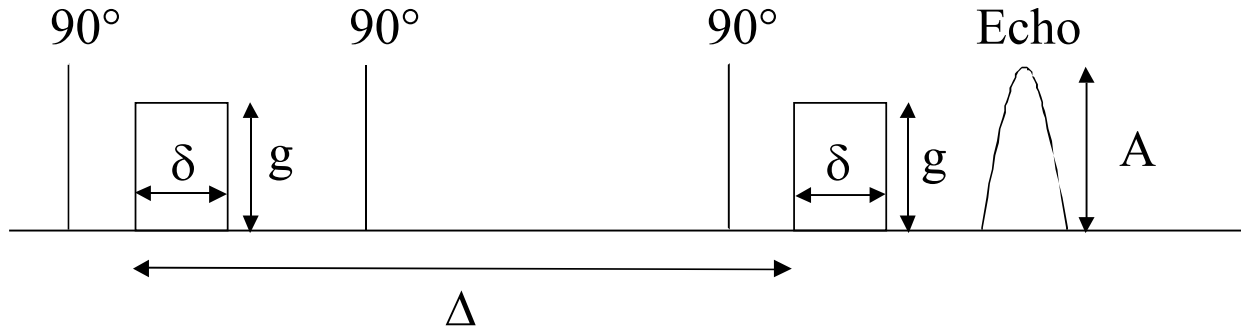
In this work, nuclear magnetic resonance (NMR) diffusion techniques have been employed to study the diffusion of methanol in Nafion 117. NMR has a number of advantages over electrochemical methods; it is a non-destructive technique that enables specific nuclei to be studied independently. It is also possible to discriminate between the same nucleus in different chemical environments. With methanol, for example, the hydroxyl protons are shifted 580Hz (in a 9.4T magnetic field) from the methyl protons. In the case of a methanol solution, both water and methanol contain hydroxyl protons, whereas the methyl protons are only found in the methanol. Therefore, by monitoring the behavior of the methyl proton peak, it is possible to study the diffusion of methanol independently of the water. Preparation of the membrane samples with a known methanol concentration, however, is no trivial matter given the volatility of the methanol. To ensure that the concentration of methanol within the membrane remains constant, the measurements were conducted with the membrane immersed in a known methanol solution throughout the entire experiment. It is clear that both the methanol in the membrane and in the solution will contribute to the NMR signal. Furthermore, the solution peak will be far more intense than the peak from the methanol within the membrane. The challenge taken up here, therefore, is to suppress the signal from the methanol in solution, thus allowing diffusion of the methanol within the membrane to be observed unambiguously. This paper will outline the methodology that enables such measurements to be performed.

## Theory and Experimental Method

Diffusion measured by NMR methods typically involves the use of two pulsed field gradients (Figure 1); the first encodes the position of the nuclei and the second detects the nuclei after a given diffusion time,  $\Delta$ . The second gradient pulse will only detect the nuclei that have not moved during the diffusion time. By measuring the signal intensity as a function of the gradient strength ( $A(g)$ ), the diffusion coefficient can be calculated from the Stejskal and Tanner equation (Stejskal and Tanner, 1965) (Eq. 1):

$$A(g) = A(0)\exp[-\gamma^2 D g^2 \delta^2 (\Delta - \delta/3)] \quad (1)$$

where  $A(0)$  is the signal intensity when the gradient is zero,  $\gamma$  is the gyromagnetic ratio,  $D$  is the diffusion coefficient,  $g$  is the gradient strength and  $\delta$  is the length of the gradient pulse. In the case of fast diffusing species, even the presence of small gradients will result in fast signal decay. On the other hand, slow diffusing species require larger gradients for the same effect. This difference in diffusion behavior can be exploited in the experiments conducted in this work in order to suppress the solution peaks and observe only the methanol within the membrane.



**Figure 1. Standard NMR pulse sequence for measuring diffusion coefficients.**

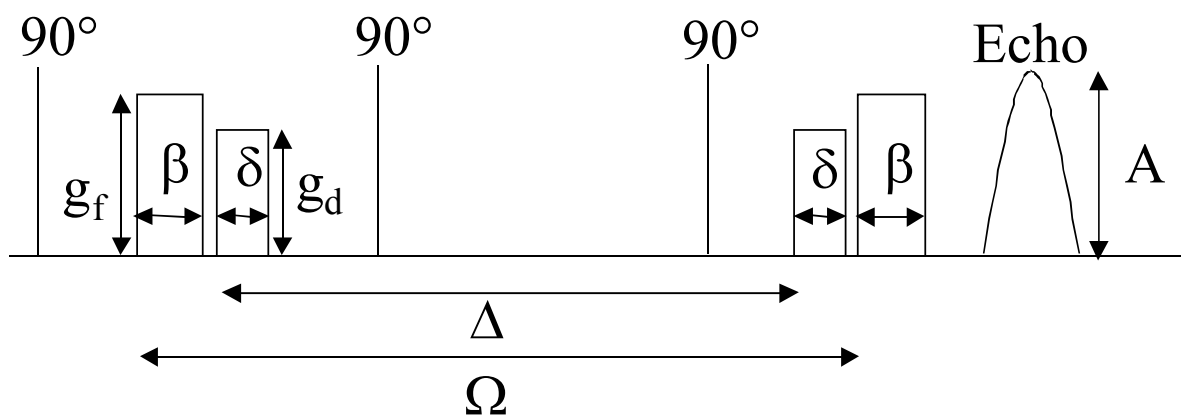
A modified pulse sequence was employed for such experiments, as show in Figure 2. By adding a second set of gradient pulses (a filter gradient), the signal from the faster diffusing species (solution) will decay more rapidly, leaving only the peak from the methanol in the membrane for analysis. With this pulse sequence, the standard Stejskal and Tanner equation (Eq. 1) is no longer applicable for calculating the diffusion coefficients due to the presence of cross terms between the filter and diffusion gradients. Mathematical analysis of these cross terms has been provided by Neeman et al. (1990), and results in the following equation (Eq. 2):

$$A(g)/A(0) = \exp[-\gamma^2 D (g_f^2 a + g_d^2 b + g_f g_d c)] \quad (2)$$

In this equation,  $g_f$  and  $g_d$  are the filter and diffusion gradient strengths, respectively, and  $a$ ,  $b$  and  $c$  are defined as:

$$a = \beta^2 (\Omega - \beta/3) \quad b = \delta^2 (\Delta - \delta/3) \quad c = 2\beta\delta\Delta$$

where  $\beta$  and  $\Omega$  are the length of the filter gradient pulses and the time between the two of them, respectively, with the other parameters defined as above. Based on this equation, there are a number of variables that can be considered when conducting this experiment; the strength and length of the filter gradient, the time between the filter and diffusion gradients and the diffusion time. Each variable will have some influence on the suppression of the solution peak, although to different extents in accordance with Eq. 2. For the work presented here, only the effect of the filter gradient strength on the signal intensity and diffusion behavior will be considered.



**Figure 2. Modified NMR pulse sequence with the addition of a second set of gradient pulses used to suppress the fast diffusing component.**

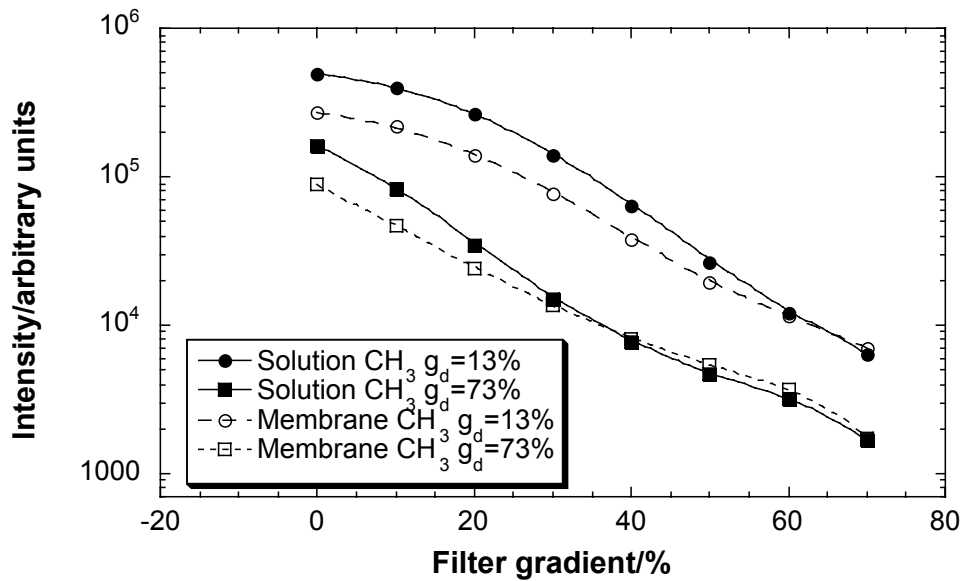
The system chosen for this study was a Nafion 117 (Du Pont) membrane immersed in an 8M methanol solution. Pretreatment of the membrane was performed according to the method described elsewhere (Ren, 2000). The membrane was immersed in the methanol solution at least 24 hours prior to performing the NMR measurements. As mentioned earlier, the measurements were conducted with the membrane continually immersed in the solution. A Bruker AMX400 spectrometer equipped with a microimaging gradient set was used to study the diffusion behavior. The maximum gradient strength was calibrated with water ( $D = 2.299 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at  $25^\circ \text{C}$  (Mills, 1973)) and found to be  $37.8 \text{ G cm}^{-1}$ . For each measurement, the diffusion gradient was varied while the filter gradient was kept constant. The signal intensity and diffusion behavior were investigated for filter gradients ranging from 0% to 70% of the maximum gradient strength at increments of 10%. The length of the filter gradient ( $\beta$ ) was 4ms, the time between the filter and diffusion gradients was 1ms and the diffusion time ( $\Delta$ ) was 20ms. All measurements were made at  $30^\circ \text{C}$  and the data analyzed with the use of Eq. 2.

## Results and Discussion

In the absence of all gradients, three proton resonances were observed corresponding to the hydroxyl protons in solution (with contribution from both the water and the methanol) and the methyl protons in both the solution and the membrane. Although partly obscured, the peak corresponding to the methyl protons in the membrane could clearly be seen as a shoulder on the side of the methyl protons in solution peak. The absolute intensity of the membrane peak will therefore be a combination of both the methanol in the membrane and in the solution. The same will also be true for the solution peak, although the membrane peak contributes to a lesser extent. The overlap of these peaks makes it difficult to measure the diffusion coefficient of the methanol in the membrane. It is highly likely, however, that both diffusion processes will influence the signal decay with increasing gradient strength. Hence, the need to suppress the solution peak is paramount.

We have proposed that the methanol solution peak can be suppressed through the use of a filter gradient in a pulsed field gradient NMR measurement. The intensities of the two methyl peaks as a function of the filter gradient strength are shown in Figure 3. When no filter gradient is present, the intensity of the solution peak is significantly greater than that of the membrane peak. As the filter gradient increase, the intensities of the two peaks approach one another before the solution peak

eventually becomes the less intense of the two peaks. It should be noted that once this occurs, it is difficult to determine the absolute intensity of the solution peak as it is now partly obscured by the membrane peak. The more rapid attenuation of the solution peak is the result of faster diffusion of the methanol in solution. Thus, it would seem that the solution peak can be suppressed if large enough filter gradients are employed (around 60%). Furthermore, the diffusion coefficient for methanol within the membrane should be measurable without ambiguity.

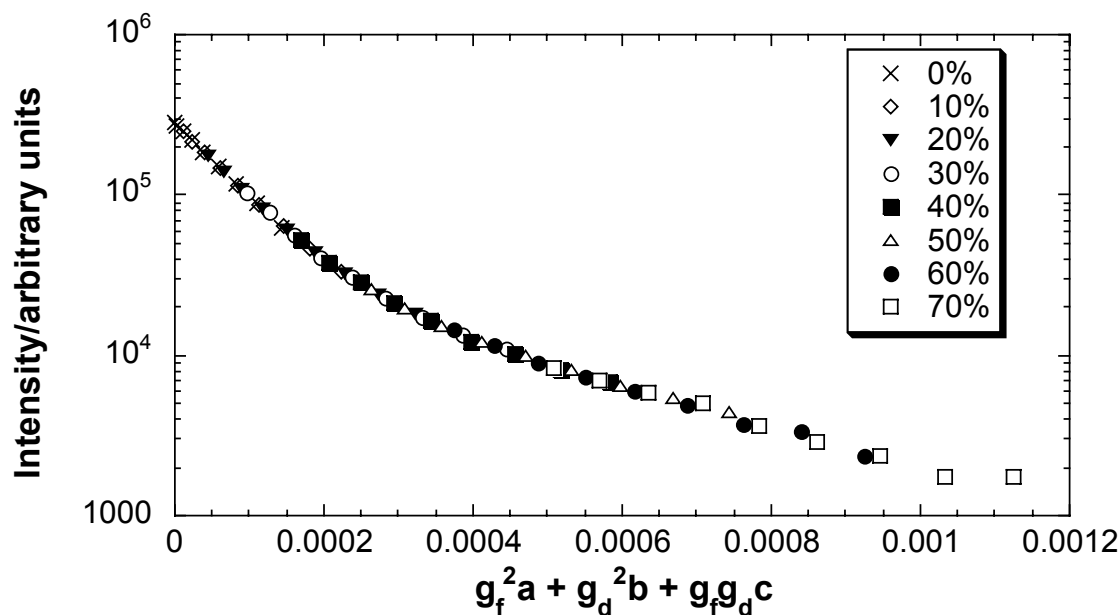


**Figure 3. The intensities of the solution and membrane peaks as a function of the strength of the filter gradient.**

The data are shown for two constant diffusion gradients, 13 and 73%.

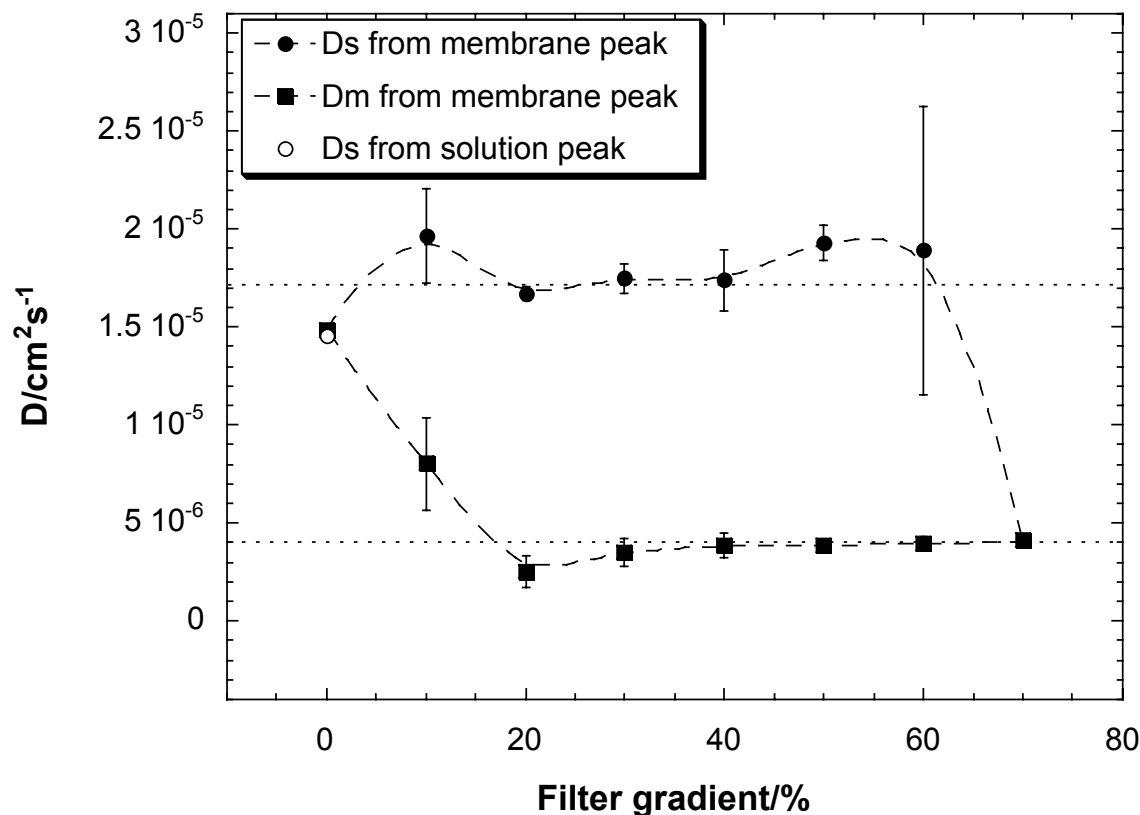
A plot of the signal intensity as a function of the combined gradients ( $g_f^2a + g_d^2b + g_fg_dc$ ) should result in a linear graph with the slope proportional to the diffusion coefficient,  $D$ . Figure 4 shows the membrane peak intensity as a function of these combined gradients for measurements performed with different filter gradient strengths. While all the data nicely lines up on the same curve, the graph is not linear, suggesting that more than one diffusion process is present. As mentioned earlier, it would seem that when the solution peak is still dominant (at low filter gradients), the membrane peak is strongly influenced by the diffusion behavior of the methanol in solution. As the filter gradient increases and the solution peak is subsequently suppressed, the diffusion of the methanol in solution has less effect on the membrane peak. Consequently, at the highest filter gradients, the behavior should solely reflect the methanol diffusion within the membrane. At intermediate filter gradients, both the methanol in solution and in the membrane should have a significant contribution to the signal intensity. Assuming the effect is additive, the data can be fitted with a double exponential (as shown in Eq. 3, where  $s$  and  $m$  refer to the solution and the membrane). The two diffusion coefficients determined from this fit should therefore be representative of the two diffusion processes.

$$A(g) = A_s(0)\exp[-\gamma^2 D_s(g_f^2a + g_d^2b + g_fg_dc)] + A_m(0)\exp[-\gamma^2 D_m(g_f^2a + g_d^2b + g_fg_dc)] \quad (3)$$



**Figure 4. The intensity of the membrane peak as a function of the combined gradients.**  
The measurements were performed for different filter gradients, ranging from 0 to 70%.

Figure 5 shows the diffusion coefficients obtained from the membrane peak as a function of filter gradient strength. The coefficient for methanol diffusion in solution, as obtained from the solution peak, is also shown for comparison. It is obvious that when there is no filter gradient (0%), the calculated diffusion coefficients are representative of the methanol diffusion in solution, even when calculated from the membrane peak. For a filter gradient of 10%, the methanol diffusion in solution still has some influence. At filter gradients of 20% and above, the methanol diffusion in the membrane approaches a relatively constant value,  $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The methanol diffusion in the solution also reaches a constant value of  $1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  between filter gradients of 20% and 40%. Upon exceeding this filter gradient, there is significant suppression of the solution signal such that the diffusion behavior begins to reflect that of the membrane.



**Figure 5. Methanol diffusion coefficients as a function of the filter gradient strength.** The coefficients were calculated from the membrane peak. The diffusion of methanol in solution, as calculated from the solution peak, is shown for comparison.

The diffusion coefficients obtained here are reasonably consistent with the values reported in the literature. Hietala et al. (2000) used pulsed field gradient NMR methods to study the methanol diffusion in solution (no membrane was present) and in PVDF-g-PSSA and Nafion 117 membranes. The membranes were immersed in a known methanol solution, but removed prior to the NMR measurement. When no membrane was present, the diffusion coefficients for the methyl and hydroxyl protons in an 8M methanol solution were found to be  $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively. For methanol diffusion within the membrane, only the diffusion behavior of the hydroxyl protons was observed with values around  $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  reported for Nafion 117. It should be noted, however, that there will be some contribution from the water in this measurement. The protons on methanol and water will in rapid exchange in this acidic environment. Thus, the somewhat high D value reflects a weighted average between two environments. Using a similar method, Ren et al. (2000) looked at the water and methanol diffusion coefficients in Nafion 117. In this case, the methanol diffusion in the membrane was determined from the methyl protons and found to have a coefficient of approximately  $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The diffusion behavior was also found to be independent of the methanol concentration. In a slightly alternative approach, Pivovar et al. (1999) studied methanol permeability in Nafion 117, where the



permeability is equal to the product of the diffusion and partition coefficients. For a methanol concentration of 8M, the permeability was determined to be  $2 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ . Although it was not possible to directly isolate the diffusion coefficient from this product, the value is very similar to the diffusion coefficients measured in this work, particularly if it is assumed that the partition coefficient is close to 1.

## Conclusions

The aim of this work was to use a modified pulsed field gradient NMR method to study the diffusion of methanol within Nafion while the membrane is continually immersed in a methanol solution. The signal from the methanol in solution can be suppressed upon the application of a filter gradient. In the absence of the filter gradient, the diffusion of methanol in the membrane is strongly influenced by the diffusion of methanol in solution. When a filter gradient of roughly 60% is applied, it is possible to suppress the solution signal completely, enabling the diffusion of the methanol within the membrane to be observed unambiguously. Under such circumstances, the diffusion coefficient was calculated to be  $4 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ . Furthermore, at intermediate filter gradients, where both the solution and membrane contribute to the signal, a double exponential equation can be used to obtain membrane diffusion coefficient values. In conclusion, the use of NMR filter gradient measurements is a valid method for studying the diffusion coefficient of methanol within fuel cell membranes.

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